from 15% methanol–85% acetone with ether. After several refractionations the most soluble fraction was recrystallized several times from the methanol–acetone mixture. Its observed rotation (0.01% solution in 20% methanol–water at 20° in a 2-dcm. tube) was +1.63°, whence $[\alpha]^{20}_{5461}$ = +8,150°. *Anal.* Found: C, 52.1; H, 4.9; H, 3.2.

***d*- and *l*-1,8-Bis-(β-hydroxy-α-naphthylideneamino)-3,6-dithiaoctane Cobaltic Bromide Dihydrates.**—Because the above described α-bromocamphor-π-sulfonates are less soluble than the corresponding bromides the following method was adopted for transformation of the *l*-base-*d*-acid salt to the *l*-base bromide, and an exactly similar method was used to convert the *d*-base-*d*-acid salt to the *d*-base bromide: The *l*-base-*d*-acid salt (1.25 g.) was dissolved in methanol (50 ml.) and water (20 ml.) and the solution heated almost to boiling. Potassium iodide (0.25 g.) was then added, a greenish-brown precipitate of the complex *l*-base iodide separating. This was collected and dissolved in a boiling mixture of methanol (80 ml.) and water (20 ml.) and a concentrated solution of silver nitrate (1.2 mols) added. The precipitated silver iodide was filtered off and sufficient potassium bromide to precipitate the excess silver added to the hot solution. After removal of the precipitated silver bromide excess potassium bromide was added to the filtrate which was then cooled. Greenish-brown needles of the active bromide separated. These were recrystallized three times from hot 50% aqueous methanol to which some potassium bromide was added before cooling. The final product formed finely felted needles m. p. 220–222° (dec.). *Anal.* Found: C, 50.4; H, 4.3; N, 4.3; Br, 12.2. The observed rotation of a 0.01% solution in 20% methanol–water at 20° in a 2-dcm. tube for the mercury green line 5461 was −2.22°, whence $[\alpha]^{20}_{5461}$ − 11,100° and $[M]^{20}_{5461}$ − 73,370°.

***d*-1,8-Bis-(β-hydroxy-α-naphthylideneamino)-3,6-dithiaoctane cobaltic bromide dihydrate** was similarly obtained in greenish-brown needles m. p. 220–222° (dec.). *Anal.* Found: C, 50.5; H, 4.4; N, 4.2; Br, 12.1. The observed rotation of a 0.01% solution in 20% methanol–water at 20° in a 2-dcm. tube for the mercury green line 5461 was +2.21°, whence $[\alpha]^{20}_{5461}$ + 11,050° and $[M]^{20}_{5461}$ + 73,040°.

**Acknowledgment.**—The authors are indebted to Miss Joyce Fildes of this University for the organic microanalyses recorded in this paper.

## Summary

1,8-Diamino-3,6-dithiaoctane has been prepared and treated with salicylaldehyde (2 mols) and with 2-hydroxy-1-naphthaldehyde (2 mols) to give the corresponding Schiff bases. These form coördination compounds with metals such as zinc, copper, nickel, iron and cobalt. The cobaltous complexes oxidize very easily in presence of acid to cobaltic salts in which the organic moiety is attached to the central cobalt atom at six points. The complex cobaltic cations so obtained are asymmetric. Resolution of these cobaltic salts has been effected. The optically active salts are distinguished by their optical stability and their tremendous molecular rotations which are higher than any previously recorded.

SYDNEY, N. S. W., AUSTRALIA RECEIVED APRIL 26, 1949

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Low Temperature, Low Pressure, Hydrogen Atom Initiated Combustion of Hydrocarbons[1]

BY ELMER J. BADIN

A study of hydrocarbon combustion initiated by atomic hydrogen has not previously been carried out, although Geib and Harteck[2] have reported that methane–oxygen and acetylene–oxygen mixtures reacted at low temperatures when mixed with hydrogen from a discharge tube. Some preliminary results on the oxidation of $C_4$-hydrocarbons have already been reported.[3] This study has been continued, since the initial experiments indicated that, under the reaction conditions used [low temperatures (20°) and low pressures (0.20–0.55 mm.)], definite information about the manner of hydrocarbon combustion could be obtained. The results of this study are reported here.

## Experimental

Experiments were carried out in an apparatus similar to that previously described.[4] Hydrocarbon and oxygen were admitted through two capillary-type flowmeters. Hydrogen was electrolyzed from a dilute sulfuric acid–water solution and passed directly into the phosphoric acid-coated discharge tube. The degree of dissociation of the hydrogen from experiments with hydrogen and oxygen alone was estimated to be of the order of 60–70%.

The two gas streams passed into a reaction trap (51 mm. o.d.) through two concentric tubes (17.5 mm. o.d. and 8.0 mm. o.d., respectively), the hydrocarbon–oxygen mixture entering through the inner tube. The inlet tubes for hydrogen and hydrocarbon–oxygen were coated with phosphoric acid. The reaction trap, condensing traps and connecting tubes were of untreated Pyrex glass.

In most experiments the gases mixed in the main reaction trap and the products were condensed in a trap (liquid nitrogen cooled) about 30 cm. removed from the point of mixing of the gases.

Analyses for liquid products (aldehydes, ketones, hydrogen peroxide, organic peroxides) were obtained by dissolving the total product at the end of an experiment in an ice–water mixture and analyzing aliquot portions.

Total aldehyde and ketone was determined by precipitation with 2,4-dinitrophenylhydrazine in 3 *M* hydrochloric

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[1] The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and with Contract N6-ori-105 with the Bureau of Aeronautics and Office of Naval Research, as coördinated by Princeton University. Acknowledgment is due Dean Hugh S. Taylor, who has general supervision of this project, and Professor Robert N. Pease.

[2] K. H. Geib and P. Harteck, *Z. physik. Chem.*, **170**, 1 (1934).

[3] E. J. Badin, THIS JOURNAL, **70**, 3965 (1948).

[4] E. J. Badin, *ibid.*, **70**, 365 (1948).

acid. The precipitate was dried and weighed. Since a mixture of carbonyl products, too small in quantity to separate by fractional distillation, was obtained, the various aldehydes and ketones were separated by fractional crystallization of the 2,4-dinitrophenylhydrazone mixture from dilute ethanol–water mixtures. In each case the compound was obtained in sufficient purity so that it could be characterized by its melting point and a mixed melting point with a pure known derivative. In the usual case the carbonyl product consisted of two compounds one of which was formaldehyde. The weight of the total 2,4-dinitrophenylhydrazone and a separate analysis for formaldehyde, thus, gave a fair quantitative estimate of the two materials present.

Formaldehyde was determined by oxidation to formic acid with 3% hydrogen peroxide in 1 *N* sodium hydroxide. The formic acid was determined gravimetrically by precipitation of mercurous chloride with mercuric chloride.

Hydrogen peroxide was determined by titration, at 5° with 0.1 *N* potassium permanganate, of a sample acidified with sulfuric acid.

Total peroxide was estimated by iodine liberation from a solution of potassium iodide in 10% acetic acid. The iodine liberated over a twenty-four-hour period was titrated with 0.1 *N* sodium thiosulfate. Excellent end-points were obtained for both the potassium permanganate and sodium thiosulfate titrations.

Water was determined by repeating the experiment, dissolving the product in anhydrous dioxane and titrating with Karl Fischer reagent using the electrometric method of Wernimont and Hopkinson.[5]

Gas samples were obtained by repeating the experiment a second time, condensing the gases in a trap and, while maintaining the trap at 0°, collecting the gases in a buret. Analyses were carried out in the usual manner, using 30% aqueous potassium hydroxide (carbon dioxide), dilute bromine water (olefins), Oxsorbent (oxygen), Cosorbent (carbon monoxide) and combustion over copper oxide at 570° (paraffins).

Infrared spectra of combustion products were obtained using a Perkin–Elmer Model 12C instrument with rock salt prism (gas phase, 10-cm. path, silver chloride windows).

Oxygen and the gaseous hydrocarbons used were of C.P. grade.

## Results and Discussion

**Isobutane Oxidation.**—The hydrocarbon most thoroughly studied was isobutane. Results in Table I show the effect of the trap position on the liquid products of combustion. Results are also shown in Table I for the hydrogen–oxygen reaction (isobutane absent) under the same conditions. For the hydrogen–oxygen reaction under these conditions, oxygen is quantitatively converted to hydrogen peroxide and water if the gases are cooled immediately in liquid nitrogen. Removal of the condensing trap to a position 30 cm. away results in essentially unchanged water formation and greatly decreased peroxide formation. At a distance of 100 cm., peroxide is eliminated. This has previously been shown to be the case when water is passed through the discharge tube.[6] The conclusion is reached that hydrogen peroxide is first formed. Failure to stabilize it immediately results in only water formation and recombination reactions to yield gaseous products.[4]

TABLE I

ISOBUTANE OXIDATION. EFFECT OF TRAP POSITION ON OXIDATION PRODUCTS (PYREX SURFACE)

| Reactants, cc. S. T. P./min. | | | | Products, cc. S. T. P./min. | | | |
|---|---|---|---|---|---|---|---|
| Pressure mm. | *i*-$C_4H_{10}$ | $O_2$ | $H_2$[a] | $H_2O$ | $H_2O_2$ | Organic peroxides | Total aldehyde + ketone[b] |
| Products condensed (−196°) 1 cm. below point of mixing of gases | | | | | | | |
| 0.36 | 4.9 | 4.9 | 14 | 2.4 | 2.7 | 0.66 | Trace |
| .27 | 0 | 4.9 | 16 | 3.0 | 3.3 | | |
| Products condensed (−196°) 30 cm. from point of mixing of gases | | | | | | | |
| 0.36 | 4.9 | 4.9 | 14 | 1.2 | 0 | 0 | 1.1 |
| .27 | 0 | 4.9 | 16 | 2.9 | 0.35 | | |
| Products condensed (−196°) 100 cm. from point of mixing of gases | | | | | | | |
| 0.36 | 4.9 | 4.9 | 14 | 1.1 | 0 | 0 | 1.2 |
| .27 | 0 | 4.9 | 16 | 2.6 | Trace | | |

[a] Hydrogen through discharge tube. [b] Acetone + formaldehyde.

A similar set of experiments for isobutane (Table I) leads to analogous results. Immediate condensation leads to hydrogen peroxide, water and organic peroxide with only a trace of acetone and formaldehyde. Removal of the trap to the 30-cm. position eliminates hydrogen peroxide and organic peroxide, but results in appreciable amounts of acetone and formaldehyde. Further removal to the 100-cm. position does not essentially change this latter result. The experiments indicate, as in the case of the hydrogen–oxygen reaction, that peroxides are first formed. Failure to stabilize these peroxides (organic as well as hydrogen peroxide) on the wall leads to the presence of acetone, formaldehyde and water in the products and the absence of peroxides. It thus seems that water, acetone and formaldehyde are formed by gas phase reactions which are admittedly strongly affected by the nature of the surface.

Further results for isobutane are shown in Table II which is essentially a material balance for the reaction. Results here as in Table I were obtained using a "conditioned" Pyrex surface for the main reaction trap. This surface was obtained by carrying out several experiments on a clean Pyrex surface until reproducible results were obtained. One of the most significant observations in Table II is that acetone and formaldehyde over a fairly wide pressure–concentration range are formed at about equal rates. Very little carbon dioxide and carbon monoxide are formed.

**Other Hydrocarbons.**—A comparison of the relative rates of oxidation of a series of paraffins and olefins using aldehyde and ketone formation as an index of reaction has been made. Table III shows the approximate relative rates of oxidation and the main products formed.

(Experiments in this series were carried out as in Table II except that a clean Pyrex surface was

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[5] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1934).

[6] W. H. Rodebush, C. R. Keizer, F. S. McKee and J. V. Quagliano, THIS JOURNAL, **69**, 538 (1947).

TABLE II

ISOBUTANE OXIDATION

Gases mixed at 20°, products condensed (−196°) 30 cm. from point of mixing, Pyrex surface

| Reactants, cc. S. T. P./min. | | | | Liquid products,[b] (cc. S. T. P./min.) | | | | | Gaseous products,[c] cc. S. T. P./min. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pressure | $i$-$C_4H_{10}$ | $O_2$ | $H_2$[a] | $H_2O$ | $H_2O_2$ | Organic peroxides | Acetone | Formaldehyde | $CO_2$ | CO | $C_nH_{2n+2}$[d] |
| 0.27 | 0 | 4.9 | 16 | 2.9 | 0.35 | | | | | | |
| .36 | 2.0 | 7.8 | 14 | 1.6 | 0.005 | Trace | 0.60 | 0.60 | 0.17 | 0.05 | 1.7 |
| .36 | 3.1 | 6.7 | 14 | 1.4 | Trace | Trace | .60 | .51 | .13 | .08 | 2.4 |
| .36 | 4.3 | 5.5 | 14 | 1.3 | 0 | 0 | .66 | .63 | .13 | .08 | 3.8 |
| .36 | 4.9 | 4.9 | 14 | 1.2 | 0 | 0 | .67 | .46 | .08 | .10 | 4.1 |
| .36 | 5.7 | 4.2 | 14 | 1.1 | 0 | 0 | .70 | .48 | .10 | .08 | 6.4 |
| .36 | 6.5 | 3.4 | 14 | 1.0 | 0 | 0 | .75 | .40 | .10 | .08 | 7.0 |
| .20 | 4.9 | 4.9 | 7 | 1.3 | 0 | 0 | .45 | .37 | .10 | .13 | 4.2 |
| .36 | 4.9 | 4.9 | 14 | 1.2 | 0 | 0 | .67 | .46 | .08 | .10 | 4.1 |
| .48 | 4.9 | 4.9 | 21 | 1.2 | 0 | 0 | .65 | .58 | .05 | .08 | 4.0 |
| .55 | 4.9 | 4.9 | 28 | 1.1 | 0 | 0 | .66 | .58 | .05 | .08 | 3.9 |

[a] Hydrogen through discharge tube. [b] Alcohols also present; traces: acids, high molecular weight oxygen-containing material, polymer. [c] Traces of olefin present. [d] Predominantly isobutane; some methane and propane.

TABLE III

RELATIVE RATES OF CARBONYL FORMATION AND PRODUCTS OF HYDROCARBON OXIDATION

Reactants: hydrocarbon 4.9 cc./min., oxygen 4.9 cc./min., hydrogen[a] 14 cc./min., pressure 0.36 mm.; gases mixed at 20°, products condensed (−196°) 30 cm. from point of mixing; clean pyrex surface.

| Hydrocarbon | Carbonyl products formed | |
|---|---|---|
| | Total cc./min. | Products |
| Methane | 0.03 | Formaldehyde |
| Propane | 0.19 | Acetaldehyde, formaldehyde |
| Propylene | 1.1 | Acetaldehyde, formaldehyde |
| $n$-Butane | 0.34 | Acetaldehyde, formaldehyde |
| Isobutane | 0.57 | Acetone, formaldehyde |
| 1-Butene | 0.98 | Propionaldehyde, formaldehyde |
| 2-Butene | 1.3 | Acetaldehyde, formaldehyde |
| Butadiene | .. | Acrolein, glyoxal, formaldehyde |

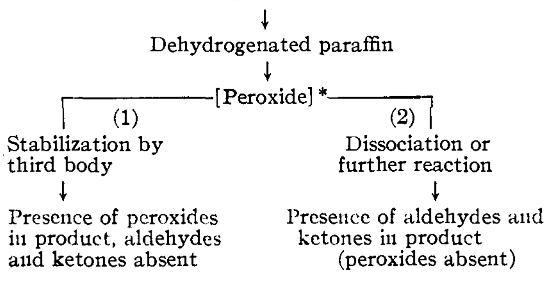
[a] Hydrogen through discharge tube.

used for each experiment. The rate for isobutane is thus lower than in Table II.) Comparison of the rates shows that methane is slowest, the paraffins (isobutane, *n*-butane and propane) are intermediate in rate of oxidation (isobutane and *n*-butane being faster than propane) and that the olefins (propylene, 1-butene and 2-butene) oxidize most rapidly, 2-butene being somewhat faster than the other olefins. These results are qualitatively in agreement with the relative rates obtained by others for the reaction of atomic hydrogen and paraffins in the absence of oxygen. Thus the activation energies for the reaction in the absence of oxygen (beyond traces) using the discharge tube method are for methane 13 ± 2 kcal., for propane 10 ± 2 kcal., for *n*-butane and isobutane 10 ± 1.5 kcal., and for propylene about 5 kcal.[7] The values for 1-butene and 2-butene would be expected to be of the same order of magnitude as for propylene. In this connection the recent work of Melville and Robb[8] is of interest in that it supplies data on the relative reactivities of H with a series of olefins.

The data in Tables II and III also supply information in regard to the initial "point of oxygen attack" in the hydrocarbon molecule. In each case about a 1:1 split of the hydrocarbon occurs to give the products. In the case of isobutane, acetone and formaldehyde result. In the case of *n*-butane, acetaldehyde seemed to be present in greater concentration than formaldehyde. Such information has been, in general, not obtained under most conditions of hydrocarbon combustion since complete degradation to formaldehyde has usually resulted. The success in the present instance of obtaining such results may be ascribed to the reaction conditions chosen. Excessive branching and degradation to formaldehyde are prevented by the wall functioning as the third body. Somewhat similar results might be expected at the other extreme of pressure (above one atmosphere) where molecules in the gas phase functioning as the third body might lead to similar observations.

## General Conclusions

The over-all mechanism of paraffin combustion based on the present work would seem to involve, first, a dehydrogenation reaction to remove hydrogen from the paraffin molecule. This is then followed by peroxide formation. The reaction can then follow one of two alternative paths, the first leading to stabilization of the peroxide, the second to dissociation or further reaction. A simplified scheme may be represented as follows denoting by an asterisk an unstable peroxide intermediate.



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(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 251-289.

(8) H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (*London*), **196**, 494 (1949).

Further reaction after steps (1) or (2) could then lead to carbon dioxide, carbon monoxide and other gaseous products. The question of whether the primary dehydrogenation involves only one hydrogen or two hydrogens in the paraffin molecule cannot be answered. Considerable evidence[9] exists that small amounts of oxygen may function as a dehydrogenating agent to yield olefins, in which case two hydrogens are removed from the paraffin. The similarity between the products formed from *n*-butane and 2-butene indicates this might be the case. That is, *n*-butane might undergo oxidation by first losing two secondary hydrogens to form, essentially, 2-butene. In addition, the first step in the reaction does not involve hydrogen atoms as such. For example, with methane in the absence of oxygen Geib and Harteck[2] observed no reaction up to 183°. Yet, with oxygen present, appreciable amounts of formaldehyde are formed at 20° (Table III). One would like to assign the steps

$$H + O_2 + W \longrightarrow HO_2 + W$$
$$HO_2 + RH \longrightarrow \text{Products}$$

to the reaction. However, under the reaction conditions it is questionable whether $HO_2$ does not immediately dissociate giving OH. It is thus not possible to distinguish between say OH and $HO_2$ as the initiating species.

Reaction path (1) is illustrated by the first set of data in Table I; path (2) by the second and third sets in Table I. The nature of the unstable peroxide intermediate is unknown. Infrared spectra of the products of isobutane combustion, in general, verified the results in Table I. The organic peroxide vapor showed strong absorption at 11.4 $\mu$ (0–0) and in other respects was similar to a known sample of *t*-butyl hydroperoxide. The conclusion was reached that the peroxide present in the product was of an R–OOH rather than R–O–O–R type. This, of course, does not fix the structure of the peroxide intermediate. This intermediate is probably of a hydroperoxide nature and as such would follow the rules of splitting as outlined in the reaction scheme of Walsh.[10]

The oxidation of the olefins, propylene, 1-butene and 2-butene probably takes place in an analogous fashion. One cannot say on the basis of the experimental evidence whether the primary step is removal of a hydrogen from, or addition of a hydrogen to, the olefin. The work of Taylor and Smith[11] on the reaction of mercury dimethyl and olefins shows that attack (by methyl) occurs at the alpha position to a double bond. In the present case the same steps might occur. The equilibrium which may be written as $-CH_2-CH=CH- \rightleftarrows -CH=CH-CH_2-$ and which might be influenced by water or traces of acid present on the surface might also apply. Further work on combustion using this method should be of importance in elucidating the exact mechanism.

## Summary

1. Results on the combustion of isobutane initiated by atomic hydrogen at 20° and 0.20–0.55 mm. pressure are reported.

2. Peroxides under these conditions are formed by a wall reaction.

3. For isobutane, primary oxidation products are acetone and formaldehyde present in approximately 1:1 ratio.

4. The oxidation is strongly dependent on the nature of the surface; water and phosphoric acid increase the rate of combustion.

5. A comparison of the relative rates and products of oxidation of methane, propane, propylene, *n*-butane, isobutane, 1-butene and 2-butene has been made.

6. Indications that the organic peroxide present in the product contains the hydroperoxide group are supplied by infrared spectra of the peroxide.

PRINCETON, N. J. RECEIVED JULY 20, 1949

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[9] See, *e. g.*, L. S. Echols and R. N. Pease, THIS JOURNAL, **61**, 208 (1939).

[10] A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946).

[11] H. S. Taylor and J. O. Smith, *J. Chem. Phys.*, **8**, 543 (1940).